

## Theoretical study on the hydration of fluorine and chlorine anions

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**1. [Introduction]** The ionic hydrogen bond, which has stronger intermolecular interaction than typical hydrogen bond, plays an important role at various biological and chemical fields such as protein folding and proton transport [1]. Meanwhile, these hydrogen bonds could help us to understand the important phenomena of ion hydration. Many efforts have been devoted to obtain the detailed structures of the halogen ion water clusters, as one of the ionic hydrogen bonded complexes, with experimental techniques and theoretical approaches [1-7]. Experimentally, vibrational spectroscopy using argon predissociation technique has provided very useful information about the fundamental and first two overtones for  $F^-(H_2O)_n$  and  $Cl^-(H_2O)_n$  ( $n=1-4$ ) clusters [2, 3]. So far, there were many studies on the equilibrium structure and harmonic vibrational analysis from *ab initio* molecular orbital (MO) calculation [4-7]. Kim *et al* found that the tetrahedral structure (Fig. 1(4(C<sub>1</sub>))) is the energetically most stable geometry for  $F^-(H_2O)_4$  cluster, while the pyramidal structure (Fig. 1(4(C<sub>4</sub>))) is preferred for other halogen ion water clusters. We note here that their results were without the basis set superposition error (BSSE) correction, which should be important for such ionic hydrogen bonded clusters. In this paper, thus, we have carried out *ab initio* MO calculations with the BSSE correction for  $F^-(H_2O)_n$  and  $Cl^-(H_2O)_n$  ( $n=1-4$ ).

**2. [Methods]** Structures and energetics of fluoride or chloride anion and water clusters are examined at MP2 and B3LYP level with basis sets of 6-311++G\*\* and aug-cc-pVDZ. All the calculations were carried out by means of the Gaussian-09 software. The convergence criterion of the calculation was set to be  $10^{-6}$  a. u., which is corresponding to the “very tight” keyword.

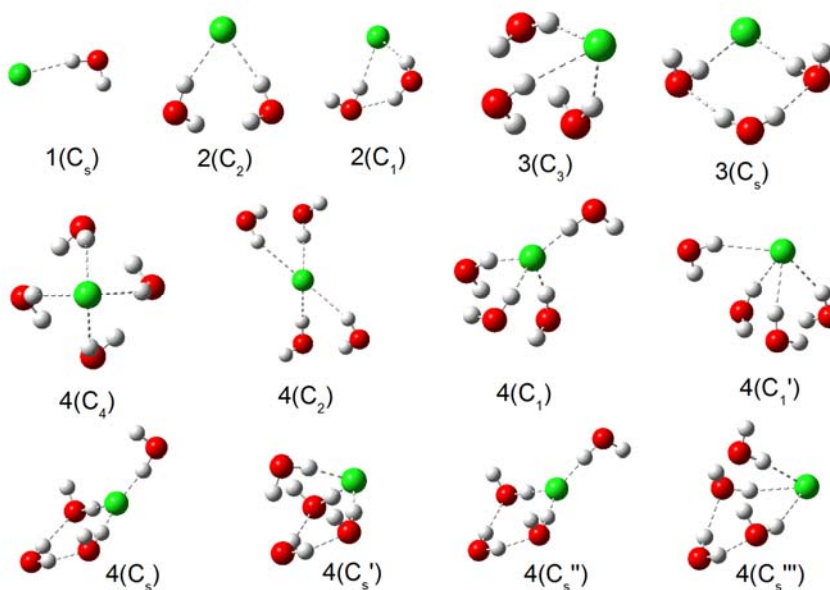


Figure 1. Optimized geometries of fluoride or chloride anion and water clusters. The color of green, red and white represents fluoride or chloride, oxygen and hydrogen atoms separately.

### 3. [Results and Discussion]

[Optimized geometries] The optimized geometries of fluoride or chloride anion and water clusters are presented in Fig. 1. The conformer number of these clusters becomes much larger when  $n=4$  than  $n=1-3$ , which indicates that the complicity of the four water case needs to be further studied. In addition, the two types of hydrogen bonds, including the one between water and anion and the one between waters, would provide us knowledge to understand the nature of hydration phenomena.

[Energetics] The binding energies of fluoride or chloride and water clusters are listed in Table. 1. The contribution of Zero point energy (ZPE) and BSSE are also shown. Without BSSE, the  $4(C_s')$  structure is the energetically most stable geometry for  $F^-(H_2O)_4$  cluster, while the tetrahedral structure  $4(C_1)$  is preferred with presence of BSSE. However, the pyramidal structure  $4(C_4)$  is preferred for  $Cl^-(H_2O)_4$  clusters for both with or without BSSE. Since the energy differences of these conformers are very small, the coexistence of these conformers is possible.

The hydrogen bond length, as well as the O-H stretching frequency, has been widely accepted to have important significance in the measure of hydrogen bond strength and dynamics. The detail of results and analysis will be presented in the poster.

Table 1. The binding energies (kcal/mol) of fluoride or chloride anion and water clusters without both ZPE and BSSE ( $\Delta E$ ) at MP2/Aug-cc-pvdz level, with ZPE ( $\Delta E_{ZPE}$ ), and with BSSE and ZPE ( $\Delta E_{BSSE+ZPE}$ ). Struc. represents the structural symmetry, and IF the number of the imaginary frequencies.

Fluoride water clusters					
n	Structure	IF	$-\Delta E$	$-\Delta E_{ZPE}$	$-\Delta E_{ZPE+BSSE}$
1	$1(C_s)$	0	26.8	26.0	24.5
2	$2(C_2)$	0	48.1	44.9	42.4
3	$3(C_3)$	0	66.9	60.4	56.2
	$3(C_s)$	0	65.4	59.3	54.9
4	$4(C_4)$	0	82.2	72.8	67.4
	$4(C_s')$	0	83.5	74.1	68.1
	$4(C_s'')$	0	81.5	73.4	68.1
	$4(C_2)$	0	81.1	73.2	68.3
	$4(C_1)$	0	82.2	73.7	68.5
Chloride water clusters					
n	Structure	IF	$-\Delta E$	$-\Delta E_{ZPE}$	$-\Delta E_{ZPE+BSSE}$
1	$1(C_s)$	0	14.7	13.5	12.6
2	$2(C_1)$	0	29.8	26.2	24.0
	$2(C_2)$	1	29.3	26.1	23.9
3	$3(C_3)$	0	46.1	39.4	35.5
	$3(C_s)$	0	43.5	37.6	34.1
4	$4(C_4)$	0	60.8	51.1	45.6
	$4(C_s')$	1	59.3	50.4	44.9
	$4(C_s''')$	0	57.5	49.1	43.9
	$4(C_2)$	0	54.5	47.2	43.0
	$4(C_1')$	0	58.2	49.5	44.4

### [References]

- [1] M. Meot-Ner, Chem. Rev., **105**, 213 (2005). [2] W. H. Robertson, *et al.*, Annu. Rev. Chem., **54**, 173 (2003). [3] E. G. Diken, *et al.*, Chem. Phys. Lett., **387**, 17 (2004). [4] S. S. Xantheas, J. Phys. Chem., **100**, 9703 (1996). [5] D. D. Kemp, *et al.*, J. Phys. Chem. A, **109**, 7688 (2005). [6] J. Baik, *et al.*, J. Chem. Phys., **110**, 9116 (1999). [7] K. S. Kim, *et al.*, J. Chem. Phys., **113**, 5259 (2000).